

## OH RADICAL MEASUREMENTS BY OPTICAL ABSORPTION SPECTROSCOPY

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The long-path absorption spectroscopy (LPA) measurement of OH utilizes the strong UV absorption spectrum of the molecule with well-resolved rotational lines around 308 nm. The OH lines  $Q_1(2)$  and  $Q_2(2)$  of the  $A^2\Sigma^+, v'=0 \leftarrow X^2\Pi_{3/2}, v''=0$  transition were selected for the detection of OH.

The light source consists of an Ar<sup>+</sup> ion laser pumped CW dye laser, the output of which is frequency doubled to emit a spectrally smooth light profile of 0.1 nm FWHM at 308 nm. This is considerably broader than the sharp (0.0018 nm wide) absorption features of OH and also wider than the total spectral region (0.06 nm) scanned around the OH lines.

For field measurements a Cassegrain-type telescope expands the small diameter of the original laser beam by a factor of 50 to about a 0.25-m diameter in order to reduce the divergence of the beam as well as its mean photon flux density, thus reducing the maximum self-generated OH concentration to  $<4 \times 10^4 \text{ cm}^{-3}$ . The light is passed into the open atmosphere and reflected at about 5 km distance resulting in a 10-km light path length. A telescope focuses the returning light onto the entrance slit of a monochromator the single exit slit of which is replaced by a mechanical scanning device operating at a scan repetition rate of 6.6 KHz. For a typical measurement (1h duration) some  $2 \times 10^7$  scans are averaged, rendering the contribution of atmospheric turbulence to the spectral noise negligible.

Noise and detection limit: Ideally, the noise should be limited by photon associated noise being proportional to  $(1/N)^{0.5}$  (N total number of photons received per wavelength interval and measuring period). However, due to laser-generated noise the level actually observed is up to one order of magnitude higher than this expectation.

For a given system noise level the sensitivity could be improved by using longer light paths, because the absorption signal is proportional to the pathlength while the system noise remains constant. However, the length of the lightpath can only be extended until the photon associated noise becomes the limiting factor. Moreover, with very long lightpaths the occasions for the OH measurement are reduced to exceptionally clear days. At a practical optimum of 10 km light path length a detection limit of  $5 \times 10^5 \text{ OH cm}^{-3}$  has been reached [Hübner et al. 1984].

Interferences: Of the several possible sources of interference with the atmospheric OH signal (solar stray light, OH radicals produced by the laser UV radiation, and narrow band ( $<0.005 \text{ nm}$ ) absorption features of other atmospheric species overlapping the

OH absorption lines) only the latter has been found to be noticeable. Absorption features due to  $\text{SO}_2$ ,  $\text{CH}_2\text{O}$  and  $\text{CS}_2$  could interfere, fortunately their superimposed spectra can be quantitatively deconvoluted, since the spectral interval contains enough significant information to unambiguously identify those absorption features, (if the gases are present in sufficient concentrations). Since known absorption features can be eliminated from the spectra  $10^6$  OH  $\text{cm}^{-3}$  would just be detectable in the presence of 22 ppb  $\text{SO}_2$  or 120 ppb  $\text{CH}_2\text{O}$ .

Presently efforts are made to increase the sensitivity of the detection by higher UV power and through better quality (spectrally smoother) laser light. Also photodiode arrays will replace the mechanical scanning technique leading to a much better light utilization due to their multiplex advantage.

Hübner, G., D. Perner, U. Platt, A. Toennissen, and D.H. Ehhalt, Groundlevel OH Radical Concentration: New Measurements by Optical Absorption, J. Geophys. Res., 89, 1309-1319, 1984